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Discreteness-of-Solvent Effects in Marcus Equations in the Mean Spherical Approximation

by

L. Blum and W.R. Fawcett

Prepared for Presentation

at

The Electrochemical Society Meeting

Washington D.C., May 1991

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In the Marcus theory of electron transfer the outer sphere contribution to the free energy of activation G_{os} is usually computed from Born continuum dielectric formula. The Mean Spherical Approximation gives systematic corrections to this quantity, which for a solvent of hard dipolar spheres can be explicitly calculated. The contributions are of two kinds: The polarization of the solvent by the charges, and the electrostriction effects, which usually are small. the effects of ion association are included using recent results for sticky potential models. These corrections also can be incorporated into the dynamical theories of solvation effects.

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The Discreteness of Solvent Effects in Marcus Equations in the Mean Spherical Approximation:

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In the Marcus theory [1] of electron transfer the outer sphere contribution to the free energy of activation ΔG_{os} is usually computed from Born continuum dielectric formula. The Mean Spherical Approximation gives systematic corrections to this quantity for molecular solvents [2]. For a solvent of hard dipolar spheres it can be explicitly calculated. The contributions are of two kinds [3]: The polarization of the solvent by the charges, and the electrostriction effects,

$$\Delta G_{os} = \Delta G_{os}^{is} + \Delta G_{os}^{ss} \qquad (1)$$

$$\Delta G_{os}^{is} = -\frac{2z_i^2 e^2 (1 - 1/\varepsilon)}{\sigma_i + \sigma_s/\lambda} \qquad (2)$$

the second term is more complex, and can be found in the literature. σ_i is the ionic diameter and σ_s is the solvent diameter. The parameter λ is obtained from the dielectric constant ε using [4]

$$\lambda(1 + \lambda)^2 = 4\sqrt{\varepsilon} \qquad (3)$$

and is related to reaction field at infinite coupling (dipole moment). The influence of ion association is included using a sticky potential approximation.
When the dipole diameter, σ_s vanishes, then the classic Born approximation is obtained.
Calculations have been carried out for a representative group of solvents. These calculations are discussed with respect to data in the literature.

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